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**C7U**  
(71) Applicant  
**Pyrene Chemical Services**  
**Limited,**  
**Ridgeway, Iver,**  
**Buckinghamshire, SLO**  
**9JJ**  
(72) Inventors  
**Guldrun Volling,**  
**Dieter Hauffe,**  
**Gerhard Muller,**  
**Werner Rausch**  
(74) Agent  
**Gill, Jennings & Every,**  
**53/64 Chancery Lane,**  
**London, WC2A 1HN**

(54) **Phosphating Compositions**

(57) Phosphate coatings are formed on metal surfaces e.g. sheet steel by use of a zinc phosphate composition having a low ratio Zn:P<sub>2</sub>O<sub>5</sub> but containing relatively high contents of ClO<sub>3</sub> and NO<sub>3</sub>. The process results in coatings having a fine grain and high wet corrosion resistance and which are

particularly suitable for immersion electro-lacquering. Solutions contain (in g/l) 0.3—1.3 Zn, 10—26 P<sub>2</sub>O<sub>5</sub>, 0.1—3 Ni, 1—6 ClO<sub>3</sub> and 5—25 NO<sub>3</sub>. The ratio of P<sub>2</sub>O<sub>5</sub>/Zn is in the range 9—85 and the ratio of Ni/Zn in the range 0—1.5. Solutions may also include sodium nitrite or nitrobenzene sulphonate, BF<sub>4</sub><sup>-</sup> or SiF<sub>6</sub><sup>2-</sup> and small amounts (e.g. up to 0.5 g/l) of other cations e.g. NH<sub>4</sub><sup>+</sup>, Ca, Mn, Cu, Co.

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## SPECIFICATION

## Process and Compositions for Coating Metal Surfaces

It is customary to provide a phosphate coating on a metal surface prior to application of a paint or other lacquer coating so as to provide corrosion resistance and increased adhesion of the lacquer to the surface. Zinc phosphate coatings are generally used, especially prior to electro-immersion lacquering. They are generally provided using aqueous zinc phosphate solution containing oxidising agents.

It has been described in German Patent Application P 22 32 067 how improved results can be obtained if the proportion of zinc is considerably reduced compared to conventional zinc dihydrogen phosphate based solutions. In particular there is described in that application solutions having a ratio be weight Zn:PO<sub>4</sub> of 1:12 to 1:10, corresponding to Zn:P<sub>2</sub>O<sub>5</sub> of 1:8.96 to 92. The reduced zinc content results in the formation of thin uniform coatings, especially on iron or steel, having improved properties. In particular they are very firmly attached and resistant and are very suitable as a base for subsequent electro-immersion lacquering.

In practice however, some difficulties can be encountered when using such low-zinc solutions. Thus under certain conditions the wet corrosion resistance is insufficient during transfer from the stage in the overall treatment when the phosphate solution is applied to the following water rinsing stage. Rust may form during transfer, in particular on portions that were incompletely contacted with the phosphating solution. For instance, treatment by immersion may have been too brief or contact with sprayed solution may have been inadequate.

A composition according to the invention suitable for forming a phosphate coating on a metal surface contains 0.3 to 1.3 parts by weight (pbw) Zn, 0 to 1.3 pbw Ni, 10 to 26 pbw P<sub>2</sub>O<sub>5</sub>, 1 to 6 pbw ClO<sub>3</sub> and 5 to 25 pbw NO<sub>3</sub> and in this composition the weight ratio Zn:P<sub>2</sub>O<sub>5</sub> is 1:9 to 85 and the weight ratio Zn:Ni is 1:0 to 1.5.

Such a composition may be provided in the form of a working solution containing water in an amount to make 1000 pbw of the composition, the solution thus containing 0.3 to 1.3 g/l Zn, 0 to 1.3 g/l Ni, 10 to 26 g/l P<sub>2</sub>O<sub>5</sub>, 1 to 6 g/l ClO<sub>3</sub> and 5 to 25 g/l NO<sub>3</sub>.

A phosphate coating may be formed on a metal surface by contacting the surface with such a solution. By the invention it is possible to obtain results as good as or better than those obtainable by the process of German Application P 22 32 067 while minimising or totally avoiding the described disadvantages of that process. In particular it is possible to obtain improved wet corrosion resistance and also improved properties when the phosphate coating is subsequently lacquered, especially by electroimmersion.

These improvements are due, at least in part, to the presence of the unusually high amounts of oxidising agents, in particular NO<sub>3</sub> and ClO<sub>3</sub>. These amounts are very much higher than would be conventional, especially bearing in mind the low content of zinc. Also it should be remembered that the chlorate is reduced to chloride during the phosphating reaction and so chloride will accumulate in the bath up to a steady state concentration.

The advantage of having the specified Zn:P<sub>2</sub>O<sub>5</sub> ratio probably follows from the fact that the zinc phosphate coating has a higher iron content and as a result is more acid resistant than when the zinc phosphate solution has a conventional, higher, zinc content. The higher acid resistance reduces the risk of loss of adhesion, for instance when the pH value decreases at the boundary surface during electroimmersion lacquering. Because of this, less coating passes into the lacquer film with consequentially reduced detrimental effect on the film. The solutions of the invention give uniformly fine coatings of low coating weight and so the electrical resistance at the boundary surface is low and subsequently applied lacquer film is very firmly adhered to the surface.

The amount of zinc in the composition is preferably 0.5 to 1.1 pbw (0.5 to 1.1 g/l working solution). The ratio Zn:P<sub>2</sub>O<sub>5</sub> is preferably 1:10 to 1:30.

Nickel may be included in the composition. It generally has a favourable effect on the rate of coating formation, especially on steel surfaces which are difficult to phosphate and on zinc surfaces. However the amount should not be more than 1.5 times the amount of zinc, for reasons of economy and increasing difficulty in operating the process.

The amount of chlorate is preferably 1.5 to 3 pbw (1.5 to 3 g/l working solution) ClO<sub>3</sub> and the amount of nitrate is preferably 10 to 20 pbw (10 to 20 g/l working solution) NO<sub>3</sub>.

It is often desirable to include alkali nitrite in the solution as an additional accelerator. The concentration expressed as NaNO<sub>2</sub> is generally between 50 and 500 mg/l, the lower to medium concentrations being preferred at treatment temperatures of 50 to 60°C while the higher concentrations are preferred at lower treatment temperatures.

Instead of using nitrite, it is often advantageous to have a nitrite free solution containing an organic nitro accelerator as an additional accelerator. A preferred material is nitrobenzenesulphonate which may be used at concentrations of 0.2 to 2 pbw (200 to 2000 mg/l) most preferably 0.3 to 0.7 pbw.

The composition may also include fluoride, which may be introduced as simple fluoride or complex fluoride or a mixture. The presence of fluoride can be advantageous when the metal surfaces are of iron or steel but is particularly desirable when zinc or aluminium surfaces are being treated. Thus

the composition may include complex fluoride, for example  $\text{BF}_4$  or, especially,  $\text{SiF}_6$ , for example in amounts of up to 1.5 pbw and/or  $\text{F}^-$ , for example in amounts of up to 0.8 pbw.

The coating solution will have its ratio of free to total  $\text{P}_2\text{O}_5$  selected for optimum coating requirements. Generally, the acid ratio is between 0.04 and 0.09, with the preferred ratio rising with increasing bath temperature, increasing total concentration and increasing amounts of zinc in proportion to  $\text{P}_2\text{O}_5$ . 5

Adjustment of the acid ratio is preferably by inclusion of alkali metal ions and preferably the compositions of the invention are substantially free of cations other than zinc, nickel if present, and alkali metals. Thus they may be totally free of other cations or may include small amounts, e.g. up to 0.5 pbw, of cations such as ammonium, calcium, manganese, copper and cobalt. The coating solutions may be formulated initially as solutions or by dilution of a concentrated composition. 10

The coating solutions are of particular value for phosphating iron or steel surfaces but are also useful for phosphating zinc and aluminium, including steel coated with zinc, zinc alloy, aluminium or aluminium alloy.

Contact of the metal surface with the solution may be effected by, for instance, spraying, flooding or immersion or a combination of such methods, for instance spraying-immersion-spraying or flooding-immersion. 15

The duration of contact is usually within conventional limits, for instance 45 seconds to 3 minutes when spraying, 2 to 5 minutes when immersing or, in a spraying-immersion-spraying process, 20 second spray, 3 minutes immersion and 20 spray. 20

The solution temperature is generally from 40 to 70°C, preferably 50 to 60°C, but temperatures as low as 30°C or lower can be used if the contact time is long enough.

The phosphate coatings produced in the invention can be used for applications for which phosphate coatings are conventionally used at present, but are of particular value as a base for electro-immersion lacquering, especially cathodic immersion electro-lacquering. In particular it is found that the coatings obtainable by the invention not only have improved wet corrosion resistance but also give improvement with certain types of lacquer as regards adhesion and lacquer film durability. This is demonstrated especially in combination tests, for instance the stone impact test combined with corrosion tests using aqueous sodium chloride solution. 25

The process of the invention is of practical application in, for instance, the phosphating of motor car bodies. 30

The following are examples of the invention.

#### Example 1

Sheet steel test bodies degreased with mildly alkaline aqueous spraying and immersion cleaning agents at 60°C and for 3 minutes were rinsed in water and then treated first for 20 seconds by spraying and after that for 180 seconds by immersion at 55°C with the following phosphating solution. 35

40	1 g/l of Zn	1.4 g/l of $\text{SiF}_6$	40
	1 g/l of Ni	0.17 g/l of F	
	0.04 g/l of $\text{FeIII}$	2 g/l of $\text{ClO}_3$	
	9.77 g/l of Na	15 g/l of $\text{NO}_3$	
	15 g/l of $\text{P}_2\text{O}_5$	0.15 g/l of $\text{NaNO}_2$	

This solution has the following titration characteristics:

45	Free $\text{P}_2\text{O}_5$ (titrate 10 ml bath sample until change of the 1st $\text{H}_3\text{PO}_4$ stage):	1.8 ml N/10 NaOH	45
	Total $\text{P}_2\text{O}_5$ (titrate 10 ml bath sample from the 1st $\text{H}_3\text{PO}_4$ stage after addition of K oxalate until change of the 2nd $\text{H}_3\text{PO}_4$ stage):	22.4 ml N/10 NaOH	
	Total Points (10 ml bath sample until change of phenolphthalein):	28.8 ml N/10 NaOH	
	Ratio of free $\text{P}_2\text{O}_5$ to total $\text{P}_2\text{O}_5$ (acid ratio):	0.08	

The test bodies were thereafter rinsed with water, after-rinsed with chromium-containing after-rinsing solution and dried. 50

The phosphate coatings covered the test bodies with a uniform grey colour, were extraordinarily finely crystalline and had a weight per unit area of 1.8 g/m<sup>2</sup>. Substantially the same coating weight and properties were obtained in those areas which, because of the particular treatment used, were treated only by immersion, and not by the spray jet. In all areas of the metal surfaces, the surfaces could be exposed for more than one minute to the vapour containing nitrite gases above the phosphating bath without incipient rusting occurring. 55

In comparative tests, when the chlorate and nitrate contents were outside the defined ranges, there was a significant tendency to rust formation especially in those areas that were treated only by immersion.

**Example 2 to 5**

A number of other bath solutions that may be formulated and used in the same manner as example 1 to obtain similar results are as follows:

<i>Example</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>
Zn (g/l)	0.8	1.0	0.8	1.0
Ni (g/l)	0.4	0.8	0.02	0.02
Na (g/l)	12.7	7.2	9.02	10.4
P <sub>2</sub> O <sub>5</sub> (g/l)	18	12	15	15
ClO <sub>3</sub> (g/l)	3	2	5	4
NO <sub>3</sub> (g/l)	20	12	10	15
Na-m-nitrobenzene-sulphonate (g/l)	0	1	0	0.5
NaNO <sub>2</sub> (g/l)	0.15	0	0.15	0
Acid ratio	~0.07	~0.08	~0.07	~0.08
Zn/Ni	1:0.5	1:0.8	1:0.025	1:0.02
Zn/P <sub>2</sub> O <sub>5</sub>	1.22.5	1:12	1:18.75	1:15

**5 Claims**

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1. A composition suitable for forming a phosphate coating on a metal surface containing 0.3 to 1.3 pbw Zn, 0 to 1.3 pbw Ni, 10 to 26 pbw P<sub>2</sub>O<sub>5</sub>, 1 to 6 pbw ClO<sub>3</sub> and 5 to 25 pbw NO<sub>3</sub> and in which the weight ratio Zn:P<sub>2</sub>O<sub>5</sub> is 1:9 to 85 and the weight ratio Zn:Ni is 1:0 to 1.5.

2. A composition according to claim 1 containing 0.5 to 1.5 pbw Zn, 1.5 to 3 pbw ClO<sub>3</sub>, and 10 to 20 pbw NO<sub>3</sub>.

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3. A composition according to claim 1 or claim 2 also containing alkali nitrite.

4. A composition according to claim 3 containing 0.05 to 0.5 pbw alkali nitrite, measured as NaNO<sub>2</sub>.

5. A composition according to claim 1 or claim 2 also containing organic nitro compound.

6. A composition according to claim 5 containing 0.2 to 2 pbw organic nitro compound.

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7. A composition according to claim 5 or claim 6 in which the organic nitro compound is a nitrobenzene-sulphonate.

8. A composition according to any preceding claim containing fluoride.

9. A composition according to claim 8 containing simple fluoride in an amount up to 0.8 pbw F<sup>-</sup>.

10. A composition according to claim 8 or claim 9 containing complex fluoride in an amount up to 1.5 pbw.

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11. A composition according to any preceding claim substantially free of cations other than zinc, nickel and alkali metal.

12. A composition according to any preceding claim in the form of an aqueous solution

containing water to make 1000 pbw.

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13. A composition according to claim 12 in which the solution has a ratio of free to total P<sub>2</sub>O<sub>5</sub> of 0.04 to 0.09.

14. A composition according to claim 1 substantially as herein described with reference to any of the Examples.

15. A process in which a phosphate coating is formed on a metal surface by contacting the surface with a composition according to claim 12 or claim 13.

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16. A process according to claim 15 in which a lacquer coating is formed over the phosphate coating by electroimmersion.

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PYRENE CHEMICAL SERVICES LTD	N/A

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**ABSTRACT:**

CHG DATE=19940730 STATUS=O> Phosphate coatings are formed on metal surfaces e.g. sheet steel by use of a zinc phosphate composition having a low ratio Zn:P2O5 but containing relatively high contacts of ClO3 and NO3. The process results in coatings having a fine grain and high wet corrosion resistance and which are particularly suitable for immersion electro-lacquering. Solutions contain (in g/l) 0.3-1.3 Zn, 10-26 P2O5, 0.1-3 Ni, 1-6 ClO3 and 5-25 NO3. The ratio of P2O5/Zn is in the range 9-85 and the ratio of Ni/Zn in

the range 0-1.5. Solutions may also include sodium nitrite or nitrobenzene sulphonate,  $\text{BF}_4^-$  or  $\text{SiF}_6^{2-}$  and small amounts (e.g. up to 0.5 g/l) of other cations e.g.  $\text{NH}_4^+$ , Ca, Mn, Cu, Co.